

The First L-Edge Spectra of Transition Metal Compounds at ALS Magnetic Spectroscopy Beamline 4.0.2

Hongxin Wang¹, Lilian Jacquamet^{1,2}, Jun Feng¹, Anthony T. Young¹,
Weiwei Gu¹, Artur Baur², and Stephen P. Cramer^{1,2}

¹Lawrence Berkeley National Lab, Berkeley, CA 94720

²Department of Applied Science, University of California, Davis, CA 95616

Unresolved oxidation state, spin states or electron density has contributed to many longstanding controversies in many Mn, Fe, Co, Ni and Cu complexes.^{1,2} In studying electronic structures, L-edge X-ray absorption spectroscopy of these transition metal complexes has demonstrated several advantages³ over the usual K-edge measurement. These features include a rich and theoretically interpretable multiplet due to the strong interaction between 2p hole and 3d electrons, a direct probe of the metal-ligand bonding orbital (3d), a dipole-allowed 2p→3d transition, and a better X-ray energy resolution. For these reasons, L-edge absorption spectroscopy is one of the best methods available now to study electronic structures various inorganic and bioinorganic complexes.^{3,4}

ALS beamline 4.0.2 is a magnetic spectroscopy undulator beamline, which has an operation energy of 20-1800 eV, a photon flux of 1×10^{13} photons/sec/0.1%BW (at 800 eV) and a resolving power of 5,000 and 10,000. It is an ideal soft X-ray beamline to measure 3d transition metal absorption and magnetic dichroism spectroscopy for various inorganic and bioinorganic applications. In a recent experiment at 4.0.2, we have measured the L-edge X-ray absorption spectra for a series of Mn, Fe, Co, Ni and Cu compounds for beamline characterization under our usual experimental conditions. We also measured battery sample LiMnO₂ from different processing conditions and obtained fruitful results.

Figure 1 shows the L-edge absorption spectrum of MnF₂ where peaks with less than 1 eV nature width has been resolved clearly. Although the absolute resolution is hard to estimate from this data alone because the accurate nature width is not available, this spectrum demonstrated better details than the spectra we took previously elsewhere. In the right panel, the spectrum of K₃[Fe(CN)₆] also exhibits a sharp absorption peak in the L₃ region. At the first L₃ absorption maximum at 706.8 eV, a total linewidth of 0.5 eV has been observed which is not available in our measurements elsewhere. In Fig. 2, we have shown the L-edge absorption spectrum of NiF₂ where a second L₃ peak has been clearly resolved. In the right panel, NiF₂ spectrum taken at 4.0.2 has demonstrated a much better resolution than the spectrum took at SSRL beamline 8.2. The comparison shows the high resolving power of the beamline 4.0.2 under our experimental conditions. The high resolution could be critical in studying less ionic chemical complex or biological molecules, such as NiFe hydrogenase,⁴ where a shoulder instead of second peak is presented and makes us harder to identify whether the second peak / shoulder is there (in order to tell whether the Ni is definitely high spin Ni(II)). In a high resolution beamline as ALS 4.0.2, this situation might be changed and more accurate and detailed Ni electronic information could become available from hydrogenases. We have planned the experiment on hydrogenases when the commissioning is over.

We have also measured CoF₂ and battery sample LiMnO₂ in this experiment, for which more analysis are required to conclude from the measurement.

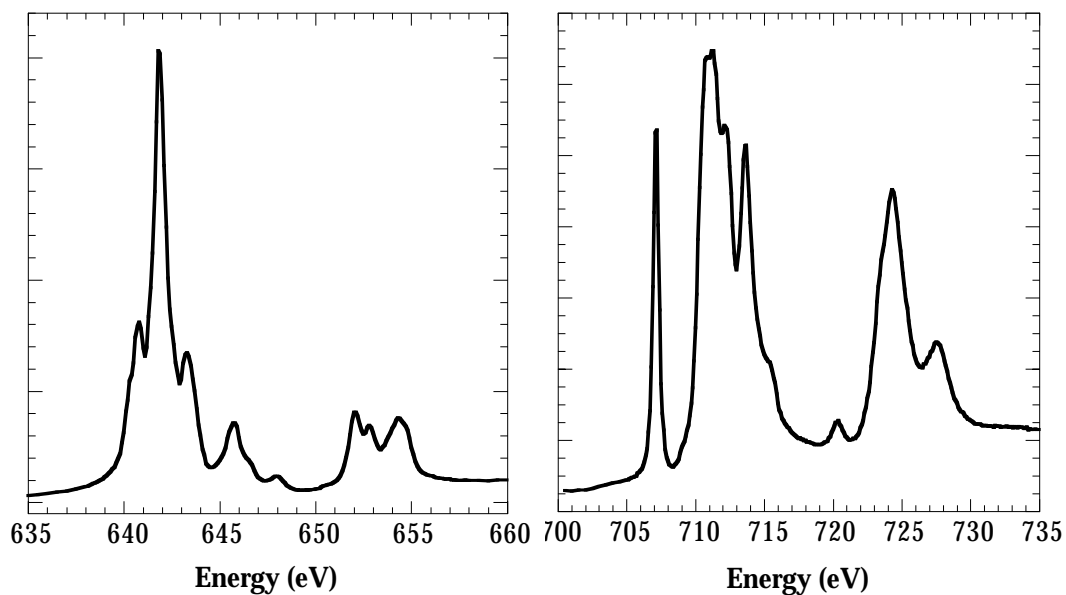


Figure 1. (Left) L-edge absorption spectrum of MnF₂; (Right) L-edge absorption spectrum of K₃[Fe(CN)₆]. Both exhibits rich multiplet structures.

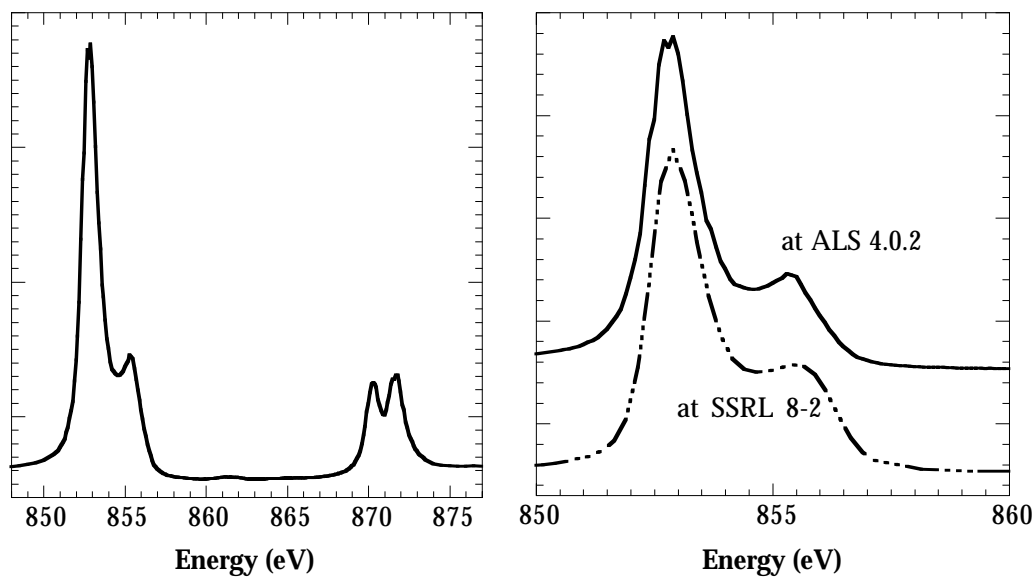


Figure 2 (Left) L-edge absorption spectrum of NiF₂; (Right) L₃ portion of the NiF₂ absorption spectrum taken at ALS 4.0.2 (solid line) versus the one taken at SSRL 8-2 (dashed line).

References

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Principal investigator: Stephen P. Cramer, Department of Applied Science, University of California, and Ernest Orlando Lawrence Berkeley National Laboratory. Davis. Email: cramer@lbl.gov. Telephone: 510-486-4720.